Supplemental Material
Synthesis of diprotected monosubstituted hydrazine derivatives from *tert*-butyl carbazates and boronic acids.

George W. Kabalka and Sankar K. Guchhait*

General Experimental Procedure:

CuCl (0.1 mmol), boronic acid (1.1 mmol) and 3 A^{o} molecular sieves (500 mg, freshly activated) were placed in an oven dried round-bottomed flask under nitrogen. Dry 1,2-dichloroethane (1.5 ml) was then added and the mixture cooled to 0 ^{o}C. Dry pyridine (4.0 mmol) was added, followed by a solution of *tert*-butyl carbazate (2.0 mmol) in dry 1,2-dichloroethane (1.5 ml). The reaction mixture was slowly allowed to attain room temperature. A balloon filled with dry air was attached to the flask and the mixture stirred for the indicated time. The resultant mixture was filtered through a short plug of silica gel to remove the copper salts and molecular sieves and the plug rinsed with ethyl acetate. The solvent was removed from the filtrate under reduced pressure and the product purified by silica gel chromatography (ethyl acetate-hexane). ^{1}H and ^{13}C NMR spectra were run in $CDCl_3$. Melting points are uncorrected.

1. 1,2-Bis(*t*-butyloxycarbonyl)-1-phenylhydrazine (entry 1) White solid, m.p.: 110-111 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.48 (s, 18H), 6.96 (br s, 1H, NH), 7.10 (t, *J* = 7.25 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.38–7.42 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 155.3, 153.5, 142.1, 128.3, 125.4, 123.5, 82.0, 81.3, 28.0. Anal. Calcd. For $C_{16}H_{24}N_2O_4$: C, 62.32; H, 7.84. Found: C, 62.48; H, 7.86.
2. 1,2-Bis(*t*-butyloxycarbonyl)-1-(4-methylphenyl)hydrazine (entry 2). White solid, m.p.: 130–131 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.48 (s, 18H), 2.30 (s, 3H, CH_3), 6.70; 6.89 (br s, 1H, NH), 7.10 (d, *J* = 8.25 Hz, 2H), 7.28 (d, *J* = 8.25 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 155.3, 153.7, 139.6, 135.3, 128.9, 123.7, 81.9, 81.3, 28.1, 20.8. Anal. Calcd. For $C_{17}H_{26}N_2O_4$: C, 63.33; H, 8.13. Found: C, 63.46; H, 8.13.
3. 1,2-Bis(*t*-butyloxycarbonyl)-1-(4-methoxyphenyl)hydrazine (entry 3). White solid, m.p.: 134 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 18H), 3.77 (s, 3H), 6.83 (d, *J* = 6.60 Hz, 2H), 6.93 (br s, 1H, NH), 7.27–7.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 155.4, 154.0, 135.3, 126.0, 113.6, 81.8, 81.2, 55.3, 28.1 Anal. Calcd. For $C_{17}H_{26}N_2O_5$: C, 60.34; H, 7.74. Found: C, 60.42; H, 7.71.
4. 1,2-Bis(*t*-butyloxycarbonyl)-1-(4-chlorophenyl)hydrazine (entry 4). White solid, m.p.: 130–131 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 18H), 6.75; 6.88 (br s, 1H, NH), 7.25 (d, *J* = 6.60 Hz, 2H), 7.35 (d, *J* = 5.70 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ155.7, 153.6, 141.0, 131.0, 128.7, 125.0, 82.9, 82.0, 28.4. Anal. Calcd. For $C_{16}H_{23}ClN_2O_4$: C, 56.06; H, 6.76. Found: C, 56.15; H, 6.86.
5. 1-(4-Bromophenyl)-1,2-bis(*t*-butyloxycarbonyl)hydrazine (entry 5). White solid, m.p.: 132 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 18H), 6.70; 6.85 (br s, 1H, NH), 7.26–7.31 (m, 2H), 7.40 (d, *J* = 6.30 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 153.5, 141.6, 131.7, 125.3, 119.2, 82.9, 82.1, 28.4. Anal. Calcd. For $C_{16}H_{23}BrN_2O_4$: C, 49.62; H, 5.99. Found: C, 49.85; H, 6.11.
6. 1,2-Bis(*t*-butyloxycarbonyl)-1-(3-nitrophenyl)hydrazine (entry 6). Yellowish white sold, m.p.: 67–68 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 18H), 7.14 (br s, 1H, NH), 7.45–7.46 (m, 1H), 7.82 (br s, 1H), 7.94–7.96 (m, 1H), 8.34 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 152.7, 148.1, 143.2, 129.0, 128.0, 119.4, 117.3, 83.3, 82.1, 28.0. Anal. Calcd. For $C_{16}H_{23}N_3O_6$: C, 54.38; H, 6.56. Found: C, 54.72; H, 6.60.
7. 1-(4-Acetylphenyl)-1,2-bis(*t*-butyloxycarbonyl)hydrazine (entry 7). White solid, m.p.: 136 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.52 (s, 18H), 2.58 (s, 3H), 6.85; 7.04 (br s, 1H, NH), 7.57 (d, *J* = 6.30 Hz, 2H), 7.91 (d, *J* = 6.30 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 155.2, 153.5, 146.2, 133.3, 128.8, 121.5, 83.0, 81.9, 28.0, 26.4. Anal. Calcd. For $C_{18}H_{26}N_2O_5$: C, 61.70; H, 7.48. Found: C, 61.90; H, 7.46.
8. 1,2-Bis(*t*-butyloxycarbonyl)-1-(2-methylphenyl)hydrazine (entry 8). White solid, m.p.: 116–117 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38–1.50 (m, 18H), 2.28 (s, 3H), 7.05–7.15 (m, 4H), 7.43 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 153.0, 140.9, 135.3, 130.2, 127.4, 126.2, 81.6, 80.9, 28.0, 17.7. Anal. Calcd. For $C_{17}H_{26}N_2O_4$: C, 63.33; H, 8.13. Found: C, 63.29; H, 8.13.
9. 1,2-Bis(*t*-butyloxycarbonyl)-1-(nonenyl)hydrazine (entry 9). Gummy liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, *J* = 5.40 Hz, 3H), 1.26–1.35 (m, 10H), 147 (s, 18H), 1.99–2.04 (m, 2H), 5.05–5.12 (m, 1H), 6.60–6.83 (m, 2H, CH and NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.1, 152.5, 125.9, 109.6, 82.0, 81.4, 32.0, 30.3, 29.6, 29.3, 29.2, 28.3, 22.8, 14.2. Anal. Calcd. For $C_{19}H_{36}N_2O_4$: C, 64.01; H, 10.18. Found: C, 63.73; H, 10.26.
10. 1,2-Bis(*t*-butyloxycarbonyl)-1-(3-thiophenyl)hydrazine (entry 10). Yellowish white solid, m.p.: 90 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (s, 18H), 6.60; 6.81 (br s, 1H, NH), 7.17–7.26 (m, 3H). ^{13}C NMR (75

MHz, $CDCl_3$): δ 155.2, 153.2, 141.0, 124.1, 122.7, 111.2, 82.7, 81.8, 28.4. Anal. Calcd. For $C_{14}H_{22}N_2O_4S$: C, 53.48; H, 7.05. Found: C, 53.69; H, 7.16.

11. 1,2-Bis(*t*-butyloxycarbonyl)-1-(2-furanyl)hydrazine (entry 11). White solid, m.p.: 68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 18H, CH_3), 6.25 (s, 1H), 6.35 (s, 1H), 6.60; 6.82 (br s, 1H, NH), 7.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.7, 152.9, 147.5, 139.1, 110.9, 103.3, 82.9, 81.6, 28.1. Anal. Calcd. For $C_{14}H_{22}N_2O_5$: C, 56.36; H, 7.43. Found: C, 56.57; H, 7.52.
12. 1-(2-Benzothiophenyl)-1,2-bis(*t*-butyloxycarbonyl)hydrazine (entry 12). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.50–1.54 (m, 18H), 6.96–7.00 (m, 2H, CH and NH), 7.19–7.30 (m, 2H), 7.57 (d, J = 7.50 Hz, 1H), 7.65 (d, J = 7.50 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 154.5, 152.0, 144.8, 138.1, 135.8, 124.2, 123.0, 122.5, 121.5, 108.4, 83.7, 82.2, 28.1. Anal. Calcd. For $C_{18}H_{24}N_2O_4S$: C, 59.32; H, 6.64. Found: C, 59.23; H, 6.63.